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STAINLESS STEEL MATERIAL HAVING EXCELLENT RUST RESISTANCE AND
PRODUCTION METHOD THEREOF
[TAISEISEI NI SUGURETA SUTENRESU KOZAI OYOBI SONO SEIHO]

YOSHIO TARUTANI

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INVENTOR(S)	(72):	YOSHIO TARUTANI
APPLICANT(S)	(71):	SUMITOMO METAL INDUSTRIES, LTD.
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Specification

1. Title of the Invention

Stainless steel material having excellent rust resistance and the production thereof

2. Scope of Patent Claims

(1) A ferritic stainless steel material having excellent rust resistance, characterized in that a ferritic stainless steel base material which contains, on a weight basis,

Al: 0.003 % or less; Si: 0.3 to 5 %;

Mn: 0.2 to 1 %; and Cr: 8 to 25 % or less;

with the balance substantially being Fe, is provided, on the surface thereof, with a single-layered or multi-layered vapor-phase plated layer which is constituted of at least one component selected from the group consisting of Al, Ti, Si, Nb, Cr, Mo, Cu, Ni, nitrides thereof and oxides thereof, and has a thickness of 200 to 30,000 Å.

(2) A ferritic stainless steel material having excellent rust resistance, characterized in that a ferritic stainless steel base material which contains, on a weight basis,

Al: 0.003 % or less; Si: 0.3 to 5 %;

Mn: 0.2 to 1 %; Cr: 8 to 25 % or less;

and at least one component selected from the following group:

Cu: 0.05 to 0.8 %; Ni: 0.05 to 0.8 %;

Nb: 0.05 to 2.0 %; and Mo: 0.05 to 3.0 %;

with the balance substantially being Fe, is provided, on the surface thereof, with a single-layered or multi-layered vapor-phase plated layer which is constituted of at least one component selected from the group consisting of Al, Ti, Si, Nb, Cr, Mo, Cu, Ni, nitrides thereof and oxides thereof, and has a thickness of 200 to 30,000 Å.

(3) A ferritic stainless steel material having excellent rust resistance, characterized in that a ferritic stainless steel base material which contains, on a weight basis,

Al: 0.1 to 4 % or less; Si: 0.3 to 5 %;

Mn: 0.2 to 1 %; and Cr: 8 to 25 % or less;

with the balance substantially being Fe, is provided, on the surface thereof, with a single-layered or multi-layered vapor-phase plated layer which is constituted of at least one component selected from the group consisting of Al, Ti, Si, Nb, Cr, Mo, Cu, Ni, nitrides thereof and oxides thereof, and has a thickness of 200 to 30,000 Å.

(4) A ferritic stainless steel material having excellent rust resistance, characterized in that a ferritic stainless steel base material which contains, on a weight basis,

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Al: 0.1 to 4 %; Si: 0.3 to 5 %;

Mn: 0.2 to 1 %; Cr: 8 to 25 % or less;

and at least one component selected from the following group:

Cu: 0.05 to 0.8 %; Ni: 0.05 to 0.8 %;

Nb: 0.05 to 2.0 %; and Mo: 0.05 to 3.0 %;

with the balance substantially being Fe, is provided, on the surface thereof, with a single-layered or multi-layered vapor-phase plated layer which is constituted of at least one component selected from the group consisting of Al, Ti, Si, Nb, Cr, Mo, Cu, Ni, nitrides thereof and oxides thereof, and has a thickness of 200 to 30,000 Å.

(5) A ferritic stainless steel material having excellent rust resistance, characterized in that a ferritic stainless steel base material which contains, on a weight basis,

Al: 0.003 % or less; Si: 0.3 to 5 %;

Mn: 0.2 to 1 %; Cr: 8 to 25 % or less;

and at least one component selected from the following group:

Cu: 0.05 to 0.8 %; Ni: 0.05 to 0.8 %;

Nb: 0.05 to 2.0 %; and Mo: 0.05 to 3.0 %;

with the balance substantially being Fe, is first subjected to a dipping process in an oxidative or peroxidative acid solution or an electrolysis in an acid solution, and is then provided, on the surface thereof, with a single-layered or multi-layered coating layer by a vapor-phase plating method, said coating

layer being constituted of at least one component selected from the group consisting of Al, Ti, Si, Nb, Cr, Mo, Cu, Ni, nitrides thereof and oxides thereof, and having a thickness of 200 to 30,000 Å.

(6) A ferritic stainless steel material having excellent rust resistance, characterized in that a ferritic stainless steel base material which contains, on a weight basis,

Al: 0.1 to 4 %; Si: 0.3 to 5 %;

Mn: 0.2 to 1 %; Cr: 8 to 25 % or less;

and at least one component selected from the following group:

Cu: 0.05 to 0.8 %; Ni: 0.05 to 0.8 %;

Nb: 0.05 to 2.0 %; and Mo: 0.05 to 3.0 %;

with the balance substantially being Fe, is first subjected to a dipping process in an oxidative or peroxidative acid solution or an electrolysis in an acid solution, and is then provided, on the surface thereof, with a single-layered or multi-layered coating layer by a vapor-phase plating method, said coating layer being constituted of at least one component selected from the group consisting of Al, Ti, Si, Nb, Cr, Mo, Cu, Ni, nitrides thereof and oxides thereof, and having a thickness of 200 to 30,000 Å.

3. Detailed Description of the Invention

(Industrial Applicability)

The present invention relates to a ferritic stainless steel material (e.g. steel plate) having excellent rust resistance and to its production method.

(Prior Art and its Problems)

Recently, in the high growth economic environment, significant diversity has been found in life styles and value concepts. For example, in spite of its high cost, the use of stainless steels, which have an attractive and deep metallic luster, have excellent corrosion resistance and provide a unique high-grade appearance, have previously been adopted for construction materials and in other fields.

However, even stainless steels having the above-described excellent properties encounter problems with local reduction of luster, so-called "staining", and red rust under severe conditions, such as in coastal areas and areas where there is volcanic ash; thus, high grade image "rust free stainless steel" may be impaired in some cases.

Various proposals for solving the above-described problem have previously been disclosed including the following techniques and methods:

a) A technique wherein an alloy element, such as Cr and Mo, having an effect of improving corrosion resistance is added as a component to stainless steel in order to improve the properties of the stainless steel itself;

b) A method which is used for a bright-annealed material, wherein the management of frost point during the bright annealing is adjusted in order to improve the corrosion resistance of the oxide film which is provided on the outermost surface; and

c) A method which is also used for a bright-annealed material, wherein a stainless steel which has previously been bright-annealed, is subjected to a passivation treatment in an oxidative acid solution;

and these techniques have been even put to practice, but the resulting effects have not been satisfactory.

Hence, in view of the above-described situation, the conclusion was reached that "the reason why the conventional prevention of "staining" is unsatisfactory is that the corrosion environment is unexpectedly severe despite the fact that the environment of the formation of "stain" is restricted to a relatively small area, which is referred to as a "stain" forming part,

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and, in order to sufficiently inhibit or prevent the formation of the "stain", a corrosion-resistance layer which is superior to conventional oxide films must be provided on the outermost surface of the stainless steel material"; following this conclusion, attempts have been made to conduct several

techniques for preventing stains and red rust, such as the following techniques:

- A) A method wherein a high corrosion resistant metal, such as Cr, is plated on the surface of a stainless steel.
- B) A method wherein an organic resin coating film is applied to the surface of a stainless steel (i.e. coating method).

Unfortunately, the former "metal plating method" is not industrially desirable, given the fact that the regulations covering the waste water treatment are going to be more strict in future, whereas the latter "organic resin coating method" may lose the characteristic metal luster and texture of stainless steels, which limits the usage of the stainless steel.

(Means of Solving the Problems)

From the above-described viewpoints, in order to solve the problems with the formation of "stains" and "red rust" without damaging the unique deep metal luster of the stainless steel and also in order to stably produce a high rust resistant stainless steel material on an industrial scale, the present inventor conducted intensive research while considering his own knowledge of corrosion-resistant coating films, which the present inventor has developed over long years of experience. As a result, the present inventor has obtained the following new findings. Specifically,

(a) Unlike conventional plating methods, the use of a vapor-phase plating method, which has been recently significantly advanced, such as a CVD (chemical vapor deposition) method, an ion plating method and a sputtering method, allows a thin film which is constituted, for example, of various metals, nitrides and oxides, to be formed on the surface of a stainless steel. Further, when a coating film which is constituted of a specific material and has a specific thickness is formed on the surface of a stainless steel by the vapor-phase plating method, the rust resistance of the resulting stainless steel can be markedly improved without impairing the unique luster of the stainless steel, thereby providing an improved prevention effect on the formation of "stains" and "red rust".

(b) However, in this case, when a commercially available conventional stainless steel material is used as a base material without any additional processes, a non-metallic inclusion which is exposed to the surface of the stainless steel material causes surface defects regardless of the type of material used for plating or of the vapor-phase plating method used, whereby a stable improvement in rust resistance cannot be expected.

(c) Further, of the non-metallic inclusions, the most common oxide-based non-metallic inclusions, particularly alumina-based non-metallic inclusions, are the most responsible for causing defects on plated films.

(d) However, a stainless steel material having excellent rust resistance can be quite stably obtained when a ferritic stainless steel material which contains a component which is appropriate for diminishing alumina-based non-metallic inclusions in the stainless steel material is used as a base material, is then optionally subjected to "a dipping process in an oxidative or peroxidative acid solution" or "an electrolysis in an acid solution" and is subjected to the above-described vapor-phase plating method.

The present invention, which is based on the above-described findings, is characterized in that:

"Excellent rust resistance is provided by producing a stainless steel material which contains:

M: 0.003 % or less, or 0.1 to 4 % (compositions are expressed by "wt %", hereinafter)

Si: 0.3 to 5 %; Mn: 0.2 to 1 %;

Cr: 8 to 25 % or less;

and at least one component selected from the following group:

Cu: 0.05 to 0.8 %, Ni: 0.05 to 0.8 %;

Nb: 0.05 to 2.0 %; and Mo: 0.05 to 3.0 %;

with the balance substantially being Fe, is provided, on the surface thereof, with a single-layered or multi-layered vapor-phase plated layer (obtained by a CVD method, an ion plating method, a sputtering method etc) which is constituted of at

least one component selected from the group consisting of Al, Ti, Si, Nb, Cr, Mo, Cu, Ni, nitrides thereof and oxides thereof, and has a thickness of 200 to 30,000 Å".

Further, the present invention is also characterized in that:

"A ferritic stainless steel material having excellent rust resistance can be stably obtained by a ferritic stainless steel base material which contains,

Al: 0.003 % or less; or 0.1 to 4 %;

Si: 0.3 to 5 %; Mn: 0.2 to 1 %;

Cr: 8 to 25 % or less;

and at least one component selected from the following group:

Cu: 0.05 to 0.8 %; Ni: 0.05 to 0.8 %;

Nb: 0.05 to 2.0 %; and Mo: 0.05 to 3.0 %;

with the balance substantially being Fe,

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is first subjected to a dipping process in an oxidative or peroxidative acid solution or an electrolysis in an acid solution, and is then provided, on the surface thereof, with a single-layered or multi-layered coating layer by vapor phase plating, said coating layer being constituted of at least one component selected from the group consisting of Al, Ti, Si, Nb, Cr, Mo, Cu, Ni, nitrides thereof and oxides thereof, and having a thickness of 200 to 30,000 Å".

Specifically, in accordance with the present invention, a high corrosion resistant coating film, which cannot be provided by a conventional plating method, is artificially formed on the surface of a specifically formulated ferritic stainless steel material by a vapor-phase plating method, whereby a stainless steel material in which the formation of "stains" can be minimized without impairing the unique luster of the stainless steel material can be obtained. The reasons that the inventive ferritic stainless steel material and its production method are restricted as described above are as follows.

(Operation)

A) Composition of Stainless Steel

(a) Al

In the present invention, it is an important requirement that the content of Al in the steel matrix (steel base material) is adjusted to be 0.003 % or less, or within a range of from 0.1 to 4 %. The content is preferably 0.002 % or less, or in a range of from 0.1 to 4 %. This is because the adjustment of the Al content is an important requirement in order to prevent alumina-based non-metallic inclusion present in the stainless steel material from being exposed to the surface and causing partial surface defects during the vapor-phase plating process, which may diminish the corrosion resistant effect.

Specifically, only the adjustment of the Al content in the steel base material to be 0.003 % or less or 0.1 or more can inhibit the formation of alumina-based non-metallic inclusions to a degree where the problem with the alumina-based non-metallic inclusions being exposed to the surface is practically not posed; thus, the rust resistance of the stainless steel material can be prevented from being impaired. When the Al content is adjusted to be 0.1 % or more, the upper limit must be set at 4 %. This is because a further improvement may not be expected if the Al content exceeds 4 % and the hot workability of the stainless steel may become markedly impaired due to an excessive addition of Al.

The above-described restriction may appear to conflict with the fact "a large amount (0.1 to 4 %) of Al is essential to diminish the formation of alumina-based non-metallic inclusions in the stainless steel", but the limitation of the improvement is assumed to be caused by the particularity of Al, which is the reduction in the deoxidizing ability due to the change in the activity coefficient Al.

In order to adjust the Al content in the steel to be 0.003 % or less, practically, it is most effective that the Al deoxidation or the addition of Al as an alloy element is not conducted during the course of the process from the period after refining process to the period of ingot casting. In particular,

not conducting the Al deoxidation is quite characteristic and effective for the production of this type of steel material.

The adverse effect of alumina-based non-metallic inclusions exposed to the surface can be efficiently diminished by a natural dipping process in an oxidative or peroxidative acid solution or an electrolysis in an acid solution, which are described later.

(b) Si

In the present invention, Si is a quite important deoxidizing element. Specifically, since "Al, which is commonly used as a deoxidizing agent for conventional steel materials" cannot be effectively used during ingoting the inventive steel material, the deoxidation in the dissolution or refining process must rely on the use of Si, whose deoxidizing effect is slightly lower than that of Al.

However, if the Si content exceeds 5 %, a further deoxidizing effect may not be expected and the hot workability of the stainless steel material can rather become markedly impaired. If the Si content is 0.3 % or less, the deoxidization may become insufficient. Therefore, the Si content is restricted to be a range of from 0.3 to 5 %.

(c) Mn

Mn immobilizes S in the stainless steel in order to ensure the hot workability; if the content is less than 0.2 %, the

intended effect may not be obtained, whereas if the content exceeds 1 %, the cold workability and formability of the stainless steel material may become impaired. Therefore, the Mn content is restricted to be a range of from 0.2 to 1 %.

(d) Cr

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Cr is the most important element in providing corrosion resistance within the inventive steel matrix (steel base material). In accordance with the present invention, the excellent rust resistance is ensured primarily by the vapor-phase plating layer which is provided on the surface of a stainless steel material, but the plating layer is so thin that matrix can be easily exposed due to scratching etc. Therefore, in order to prevent the exposure of the matrix, sufficient corrosion resistance must be provided on the steel matrix as well and, from this viewpoint, Cr plays an important role.

However, if the Cr content is less than 8 %, corrosion resistance on the scratched portion of the stainless steel material and the edge portions of the stainless steel material may not be sufficiently ensured, whereas if the Cr content exceeds 25 %, in the inventive steel material, which provides rust resistance under a variety of atmospheric exposure conditions, a further improvement in the effect may not be

clearly obtained; thus, the Cr content is restricted to be a range of from 8 to 25 %.

(e) Cu, Ni, Nb and Mo

Any of Cu, Ni, Nb and Mo have an improvement effect on the corrosion resistance of the steel base material (matrix) and can be optionally used singly or in combinations of two or more in order to prevent the rust resistance from being impaired on the scratched portion of the plated coating film. The followings are the reasons for limiting the content of each component.

Cu

Cu is an effective element for improving the corrosion resistance of the steel base material; in order to obtain the effect clearly, the content must be 0.05 % or more. If the content exceeds 0.8 %, the impairment of the corrosion resistance due to the formation of intermetallic compounds may be manifested. The Cu content is restricted to be a range of from 0.05 to 0.8 %.

Ni

Similarly to Cu, Ni is also an effective element for improving the corrosion resistance of the steel base material; in order to obtain the effect clearly, the content must be 0.05 % or more. Even if the content exceeds 0.8 %, a further improvement of the corrosion resistance may not be obtained. The Ni content is restricted to be a range from 0.05 to 0.8 %.

Nb

Nb stabilizes C in the stainless steel material and, further, improves the corrosion resistance of the stainless steel material. In particular, in the presence of Cu or Ni, a synergistic effect can be expected and thus the corrosion resistance of the stainless steel material can be further improved.

In order to desirably ensure the effect of Ni on stabilizing Cu in the stainless steel material, the content must be 0.05 % or more; however, if the content exceeds 2.0 %, the desirable impairment of the stabilizing effect on C and the corrosion resistance may not be manifested and further, the corrosion resistance may become impaired due to the formation of the Laves phase. The Nb content is restricted to be in a range from 0.05 to 2.0 %.

Mo

As well as Cr, Mo is also an effective element for improving the corrosion resistance of the steel base material; if the content is less than 0.05 %, the improvement in the corrosion resistance may not be clearly obtained, whereas if the content exceeds 3.0 %, a further improvement in the weather resistance, which the inventive steel material intends to improve, may not be expected. Therefore, the Mo content is restricted to be a range from 0.05 to 3.0 %.

(f) Other components

S, which is present as an impurity element in the stainless steel material, forms an Mn-based sulfide in the stainless steel material, resulting in causing the surface defect during the vapor-phase plating process and also resulting in the corrosion resistance of the matrix becoming impaired. For the above-described reason, it is preferred that the content of S in the stainless steel material is as small as possible. Since the surface defects can be hardly caused on the vapor-phase plated film at a content of S being 0.005 % or less, it is preferred that the content in the stainless steel material is 0.005 % or less.

B) Thickness of vapor-phase plating layer

A vapor-phase plating layer can be constituted of one or more component selected from the group consisting of Al, Ti, Si, Nb, Cr, Mo, Cu, Ni, nitrides thereof and oxides thereof. The vapor-phase layer can be a single-layered coating layer or can also be a multi-layered coating layer.

In this case, if the thickness of the vapor-phase plating layer is less than 200 Å, a uniform plating surface (deposition surface) may not be obtained and the impairment in the corrosion resistance on the defected part of the plating layer may be clearly observed, whereas if the thickness exceeds 30,000 Å, cracking or peeling-off of the plating coating film may be

caused at the bend portion of the stainless steel material. Therefore, the thickness of the vapor-phase plating layer is restricted to be a range from 200 to 30,000 Å.

In order to stably obtain a vapor-phase plating layer which is almost free of defects on the surface of a ferritic stainless steel material,

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it is advantageous that a dipping process in an oxidative or peroxidative acid solution or an electrolysis in an acid solution is conducted as a pre-treatment. The pre-treatment not only dissolves the alumina-based non-metallic inclusions exposed to the surface of a stainless steel material, thereby avoiding the adverse effect, but also strongly immobilizes the area surrounding of each of the non-metallic inclusions, thereby minimizing the impairment of the corrosion resistance of a vapor-phase plating-coated steel material caused by the presence of the non-metallic inclusion.

Examples of recommended oxidative acid solutions for diminishing or detoxifying alumina-based non-metallic inclusions exposed to the surface of a stainless steel material include a "30 % nitric acid aqueous solution". Examples of recommended peroxidative acid solutions for the same purpose include "a nitric acid aqueous solution containing hydrogen peroxide". Any

conventional acid solutions for conventional electrolysis can be used for the electrolysis according to the present invention.

The present invention is described in greater detail below with reference to embodiments.

(Embodiments)

Embodiment 1

First, ferritic stainless steel plates which were constituted of, respectively, stainless steels A, B and H to K, which were not subjected to an Al deoxidizing treatment in the refining process, stainless steels E to G, which contain a large amount of Al as a result of non-metallic inclusion floating treatment and a vacuum deoxidizing treatment in an RH furnace, and stainless steels C and D, which were subjected to an Al deoxidizing treatment, were prepared as shown in Table 1.

Thereafter, the resulting ferritic stainless steel plates were subjected to an electrolysis in a 30 % nitric acid aqueous solution at a temperature of 60 degrees Celsius in order to adjust the surface properties (vapor-phase pre-treatment) and were then plated with SiNx ($x \approx 1.35$) at a thickness of 600 Å by a sputtering process. During the sputtering process, the heated steel base plate was maintained at a temperature of 300 degrees Celsius.

Subsequently, two test pieces were obtained from each ferritic stainless steel plate thus obtained were used to

measure the pitting potential and evaluate the rust resistance, with the results being shown in Table 2. The evaluation of the rust resistance was conducted by the standard shown in Table 3, with the corresponding scores being shown in Table 2.

As is clear from the results shown in Table 2, any of the inventive ferritic stainless steel plates thus obtained showed excellent rust resistance,

Table 1

Types		Chemical Composition (wt %)											
		C	Si	Mn	P	S	Cr	Al	Cu	Ni	Nb	Mo	Fe and impurities
Embodiments	A	0.002	0.52	0.35	0.020	0.001	19.2	0.001	0.03	0.03	-	-	Balance
	B	0.003	0.55	0.32	0.026	0.001	19.2	0.001	0.51	0.24	-	-	Balance
Comparative Example	C	0.005	0.34	*0.18	0.026	0.002	18.9	*0.006	0.47	0.22	-	-	Balance
	D	0.004	0.36	*0.18	0.026	0.001	19.0	*0.077	0.47	0.20	-	-	Balance
Embodiments	E	0.002	0.47	0.33	0.025	0.001	18.9	0.121	0.48	0.20	-	-	Balance
	F	0.005	0.52	0.32	0.026	0.002	19.1	0.98	0.48	0.21	-	-	Balance
	G	0.004	0.53	0.32	0.025	0.001	19.1	2.49	0.49	0.18	-	-	Balance
	H	0.003	0.48	0.30	0.020	0.001	19.2	0.001	0.52	0.02	-	-	Balance
	I	0.001	0.50	0.32	0.021	0.001	19.2	0.001	0.03	0.50	-	-	Balance
	J	0.004	0.50	0.31	0.021	0.001	19.3	0.001	0.04	0.02	0.53	-	Balance
	K	0.002	0.51	0.33	0.021	0.001	19.3	0.001	0.03	0.03	-	2.11	Balance

Note: "*" refers to the composition being outside the range specified by the present invention.

Table 2

Test No.		Sample	Vapor-phase plating (deposition) material	Plating pre-treatment	Thickness of plating layer (Å)	Temperature of base material during sputtering (°C)	Pitting potential (60°C, 0.01M NaCl, vs. SCE)		Rust resistance (Rating after exposure to atmosphere for 6 months)	
							Sample piece 1	Sample piece 2	Sample piece 1	Sample piece 2
Embodiment	1	A	SiN _x	Treated (Electrolysis in nitric acid aqueous solution)	600	300	> 900 mV	> 900 mV	10	10
	2	B					> 900 mV	> 900 mV	10	10
Comparative Example	3	*C					364 mV	433 mV	4	4
	4	*D					565 mV	399 mV	4	4
Embodiment	5	E					> 900 mV	> 900 mV	10	10
	6	F					> 900 mV	> 900 mV	10	10
	7	G					> 900 mV	> 900 mV	10	10
	8	H					> 900 mV	> 900 mV	10	10
	9	I					> 900 mV	> 900 mV	10	10
	10	J					> 900 mV	> 900 mV	10	10
	11	K					> 900 mV	> 900 mV	10	10

Note: "*" refers to the composition being outside the range specified by the present invention.

Table 3

Rating of rust resistance	Degree of the formation of rust by exposure to atmosphere		Rating of rust resistance	Degree of the formation of rust by exposure to atmosphere	
10	No rust	Good rust resistance ↑	5	Slight red rust spots	↓ Poor rust resistance
9	Extremely slight "stains"		4	Red rust spots	
8	Extremely slight "stains"		3	Red rust spots	
7	Slight "stains"		2	Overall red rust spots	
6	Slight "stains"		1	Overall red rust	

while Comparative Examples 3 and 4, whose compositions were outside the range specified by the present invention, had poor rust resistance.

Further, in Comparative Examples 3 and 4, which used Al deoxidized stainless steels, many alumina-based non-metallic inclusions which have been elongated in the rolling direction were observed as a "linear non-metallic inclusion group" on the surface of the stainless steel, and many surface defects due to the alumina-based non-metallic inclusions were observed on the surface after sputtering.

Hence, Embodiments 5 to 7 showed desired results in spite of the Al content in the base material being in a range of from 0.121 to 2.49 %, which implies an assumption that the formation of alumina-based non-metallic inclusions was diminished by the "reduced deoxidizing ability of Al" by the addition of a large amount of Al. In fact, the amount of alumina-based non-metallic inclusions in the base materials was almost equal to that of Embodiments 1 and 2 and 8 to 11, which used stainless steels which were not Al deoxidized.

In addition, the results of the test also show that "by industrially easy process where the Al content in the base material is adjusted to be in a specific range, alumina-based non-metallic inclusions can be necessarily and sufficiently

controlled to be within a level at which the rust resistance of the vapor-phase plating plate is not impaired".

Embodiment 2

A ferritic stainless steel plate which was constituted of a stainless steel L as shown in Table 4 which had not been subjected to Al deoxidation but had been subjected to a non-metallic inclusion floating treatment and a vacuum deoxidizing treatment in an RH furnace was prepared.

Subsequently, a plurality of test pieces were obtained from the resulting stainless steel plate, were partially subjected to a degreasing treatment and then coated with SiO_x ($x \approx 2$) to a varying thickness by sputtering as shown in Table 5. During the sputtering process, the heated steel base plate was maintained at a temperature of 300 degrees Celsius.

The resulting vapor-phase plated ferritic stainless steel plate thus obtained was used to measure the pitting potential and evaluate the rust resistance as well as the presence of cracking on the vapor-phase plated coating film on 10 t-bending, with the results being shown in Table 5.

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Table 4

Types		Chemical Composition (wt %)											
		C	Si	Mn	P	S	Cr	Al	Cu	Ni	Nb	Mo	Fe and impurities
Embodiments	L	0.012	0.53	0.28	0.028	0.002	9.8	0.001	0.52	0.15	-	-	Balance

Table 5

Test No.		Sample	Vapor-phase plating (deposition) material	Plating pre-treatment	Thickness of plating layer (Å)	Temperature of base material during sputtering (°C)	Pitting potential (60°C, 0.01M NaCl, vs. SCE)		Rust resistance (Rating after exposure to atmosphere for 6 months)		Crack on 10-t bending test
							Sample piece 1	Sample piece 2	Sample piece 1	Sample piece 2	
Comparative Example	1	L	SiO _x	Not treated	* 40	300	40 mV	43 mV	2	1	No crack
	2				* 80		242 mV	258 mV	5	5	No crack
	3			Treated (Degreasing)	* 80		381 mV	423 mV	6	6	No crack
	4				200		687 mV	705 mV	9	9	No crack
Embodiment	5				400		879 mV	> 900 mV	9	10	No crack
	6				800		> 900 mV	> 900 mV	10	10	No crack
	7				1500		> 900 mV	> 900 mV	10	10	No crack
	8				400		> 900 mV	> 900 mV	10	10	Micro cracks
	9				8000		> 900 mV	> 900 mV	10	10	Micro cracks
	10				15000		> 900 mV	> 900 mV	10	10	Micro cracks
	11				28000		> 900 mV	> 900 mV	10	10	Micro cracks
	12				32000		> 900 mV	> 900 mV	10	10	Large cracks
	13										
	2										
	3										
C	2										
	3										

Note 1: "C" refers to "Comparative Example".

Note 2: "*" refers to the composition being outside the range specified by the present invention.

As is also clear from the results shown in Table 5, any of the inventive ferritic stainless steel plates showed desired

rust resistance while Comparative Examples 11, 12 and 23, whose compositions were outside the range specified by the present invention, had poor rust resistance or easily formed cracks on the surface during molding.

In the sputtering process, it is assumed that deposition of SiO_x on the base material is initiated by the formation of island-shaped depositions, with the progress not being uniform, and the island-shaped depositions are gradually enlarged to the entire surface of the base material. This tendency was also seen in the present embodiments and, in the case of the deposited film (plated film) being thin, a "tendency of the improvement level of the rust resistance being impaired due to the defects of the deposited film" was observed. Further, this tendency was expected to be remedied to some extent by increasing the temperature of the deposited base material (base material), but the actual remedying effect was not as great as expected. The rust resistance became stabilized only from a film thickness at 200 Å. There was no noticeable difference in this tendency between the above-described case and the case of using another vapor-phase plating material (deposition material).

Further, as the thickness of the deposition film (plating film) increased, cracking on the vapor-phase plating film was formed more easily, which was assumed to be caused by the temperature difference between the deposition process and the

cooling process or for the internal stress of the vapor-phase plating material (deposition material). In particular, this tendency was markedly observed when then the thickness exceeded 30,000 Å, whereby the stainless steel plates were no longer able to be put to practical use.

The adhesion of the vapor-phase plating film was greatly influenced by the degreasing process which was conducted prior to the sputtering process; therefore, it was found that degreasing must be conducted sufficiently.

Embodiment 3

As shown in Table 6, ferritic stainless steel plates which were constituted of a stainless steel M which had been subjected to Al deoxidation during the refining process and stainless steels N to P which had not been subjected to Al deoxidation, respectively, were prepared.

Thereafter, the resulting ferritic stainless steel plates were subjected to a dipping process in a 30 % nitric acid aqueous solution at a temperature of 60 degrees Celsius in order to adjust the surface properties (vapor-phase pre-treatment) and were then plated with various metals by sputtering as shown in Table 7. During the sputtering process as well, the heated steel base plate was maintained at a temperature of 300 degrees Celsius.

Table 6

Types		Chemical Composition (wt %)											
		C	Si	Mn	P	S	Cr	Al	Cu	Ni	Nb	Mo	Fe and impurities
Embodiments	M	0.005	*0.28	*0.16	0.025	0.002	16.8	*0.008	0.03	0.03	-	-	Balance
Comparative Example	N	0.005	0.53	0.35	0.025	0.001	16.8	0.001	0.08	0.02	-	-	Balance
	O	0.005	0.51	0.33	0.027	0.001	20.3	0.001	0.53	0.08	0.53	0.82	Balance
	P	0.004	0.53	0.29	0.026	0.001	22.3	0.001	0.51	0.45	0.55	1.13	Balance

Note: "*" refers to the composition being outside the range specified by the present invention.

Table 7

Test No.		Sample	Vapor-phase plating (deposition) material	Thickness of plating layer (Å)	Temperature of base material during sputtering (°C)	Pitting potential (60°C, 0.01M NaCl, vs. SCE)		Rust resistance (Rating after exposure to atmosphere for 6 months)	
						Sample piece 1	Sample piece 2	Sample piece 1	Sample piece 2
Comparative Example	24	*M	SiOx	* 40	300	0.33 V	0.28 V	4	3
	25		(Lower layer) Ni, (Upper layer) SiOx	* 100		0.35 V	0.38 V	5	5
	26		(Lower layer) Cu, (Upper layer) SiOx	600		0.36 V	0.33 V	4	4
	27		(Lower layer) Ni, (Upper layer) TiNx	500		0.38 V	0.42 V	5	4
	28		Nb.NbOx	1000		0.56 V	0.36 V	4	5
	29		(Lower layer) Cr, (Upper layer) Mo	800		0.53 V	0.63 V	6	5
Embodiment	30	N	SiOx	400		0.89 V	> 0.9 V	10	10
	31		(Lower layer) Ni, (Upper layer) SiOx	450		> 0.9 V	> 0.9 V	10	10
	32		(Lower layer) Cu, (Upper layer) SiOx	600		> 0.9 V	> 0.9 V	10	10
	33		(Lower layer) Ni, (Upper layer) SiNx	450		> 0.9 V	> 0.9 V	10	10
	34		(Lower layer) Cu, (Upper	600		> 0.9 V	> 0.9 V	10	10

		layer) SiNx							
	35	(Lower layer) Ni, (Upper layer) TiNx	500			> 0.9 v	> 0.9 v	10	10
	36	Nb.NbOx	1000			> 0.9 v	> 0.9 v	10	10
	37	(Lower layer) Cr, (Upper layer) Mo	800			> 0.83 v	> 0.85 v	10	10
	38	(Lower layer) Crx.Mox, (Upper layer) Nb.NbOx	1200			> 0.9 v	> 0.9 v	10	10
	39	(Lower layer) Cu.CuOx, (Upper layer) Nb.NbOx				> 0.9 v	> 0.9 v	10	10
	40	(Lower layer) Al (Intermediate layer) Al.Al.Ox (Upper layer) AlOx	6000			> 0.9 v	> 0.9 v	10	10
	41	P	5000			> 0.88 v	0.86 v	10	10
	42	Ti				> 0.9 v	> 0.9 v	10	10

Note: "*" refers to the composition being outside the range specified by the present invention.

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Subsequently, the resulting ferritic stainless steel plate thus obtained were used to measure the pitting potential and evaluate the rust resistance by the same methods as in Embodiment 1, with the results being shown in Table 7.

As is also clear from the results shown in Table 7, any of the inventive ferritic stainless steel plates showed desired rust resistance while Comparative Examples 24 to 29, whose compositions were outside the range specified by the present invention, had poor rust resistance.

Further, it was observed that the formation of multiple plating layers (deposition layers) produced a synergistic effect not only in terms of improving the corrosion resistance of the vapor-phase plated ferritic stainless steel plate but also for improving the adhesion of the deposition materials. In particular, it was found that the formation of an Ni or Cu base layer was effective.

Furthermore, in the above embodiments, sputtering was used for the vapor-phase plating method, but it is confirmed that other deposition techniques, such as a CVD method and an ion plating method, can also be used and similar desired results can be obtained.

(Effect of the Invention)

As described above, the present invention can stably provide a highly rust resistant ferritic stainless steel material which has superior rust resistance to conventional materials and can be applied to a wide variety of fields, such as automotive moldings and exterior or interior construction materials in order to markedly improve the values and functions; therefore, the present invention provides an industrially significant effect.

STAINLESS STEEL STOCK EXCELLENT IN RUST RESISTANCE AND ITS PRODUCTION

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Publication date: 1990-05-09
Inventor: TARUYA YOSHIO
Applicant: SUMITOMO METAL IND
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- european:
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Abstract of JP2122064

PURPOSE: To stably manufacture a stainless steel stock having superior rust resistance by treating a ferritic stainless steel stock with a specific composition with oxidizing acid and then forming a vapor plating phase of Al, etc., of a specific thickness on the surface of the above stock. **CONSTITUTION:** A ferritic stainless steel stock which has a composition consisting of, by weight, $\leq 0.003\%$ Al, 0.3-5% Si, 0.2-1% Mn, 8-25% Cr, and the balance essentially Fe and further containing, if necessary, one kind among 0.05-0.8% Cu, 0.05-0.8% Ni, 0.05-2.0% Nb, and 0.05-3.0% Mo is subjected to either of immersion treatment in a solution of oxidizing acid (e.g., about 30% aqueous solution of nitric acid) or peroxidizing acid and electrolytic treatment in an acid liquor. Subsequently, a coating layer in a state of single or double layer consisting of one or more kinds among Al, Ti, Si, Nb, Cr, Mo, Cu, Ni, and the nitrides and oxides thereof is formed to 200-30000 Angstrom thickness on the surface of the above steel stock by means of vapor plating.

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⑮ 発明の名称 耐錆性に優れたステンレス鋼材及びその製法

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⑱ 発 明 者 樽 谷 芳 男 大阪府大阪市東区北浜5丁目15番地 住友金属工業株式会社内

⑲ 出 願 人 住友金属工業株式会社 大阪府大阪市東区北浜5丁目15番地

⑳ 代 理 人 弁理士 今 井 毅

明 細 書

1. 発明の名称

耐錆性に優れたステンレス鋼材及びその製法

2. 特許請求の範囲

(1) 重量割合にて

Al: 0.003%以下, Si: 0.3~5%,

Mn: 0.2~1%, Cr: 8~25%以下

を含有し、残部が実質的にFeであるフェライト系ステンレス鋼基材表面に、Al, Ti, Si, Nb, Cr, Mo, Cu, Ni及びこれらの窒化物並びに酸化物のうちの1種以上で構成され、かつ厚さ: 200~30000Åの単層又は複層の気相メッキ層を有して成ることを特徴とする、耐錆性に優れたフェライト系ステンレス鋼材。

(2) 重量割合にて

Al: 0.003%以下, Si: 0.3~5%,

Mn: 0.2~1%, Cr: 8~25%以下

を含有すると共に、更に

Cu: 0.05~0.8%, Ni: 0.05~0.8%,

Nb: 0.05~2.0%, Mo: 0.05~3.0%

のうちの1種以上をも含み、残部が実質的にFeであるフェライト系ステンレス鋼基材表面に、Al, Ti, Si, Nb, Cr, Mo, Cu, Ni及びこれらの窒化物並びに酸化物のうちの1種以上で構成され、かつ厚さ: 200~30000Åの単層又は複層の気相メッキ層を有して成ることを特徴とする、耐錆性に優れたフェライト系ステンレス鋼材。

(3) 重量割合にて

Al: 0.1~4%, Si: 0.3~5%,

Mn: 0.2~1%, Cr: 8~25%以下

を含有し、残部が実質的にFeであるフェライト系ステンレス鋼基材表面に、Al, Ti, Si, Nb, Cr, Mo, Cu, Ni及びこれらの窒化物並びに酸化物のうちの1種以上で構成され、かつ厚さ: 200~30000Åの単層又は複層の気相メッキ層を有して成ることを特徴とする、耐錆性に優れたフェライト系ステンレス鋼材。

(4) 重量割合にて

Al: 0.1~4%, Si: 0.3~5%,
Mn: 0.2~1%, Cr: 8~25%以下

を含有すると共に、更に

Cu: 0.05~0.8%, Ni: 0.05~0.8%,
Nb: 0.05~2.0%, Mo: 0.05~3.0%

のうちの1種以上をも含み、残部が実質的にFeであるフェライト系ステンレス鋼基材表面に、Al, Ti, Si, Nb, Cr, Mo, Cu, Ni及びこれらの窒化物並びに酸化物のうちの1種以上で構成され、かつ厚さ: 200~30000Åの単層又は複層の気相メッキ層を有して成ることを特徴とする、耐錆性に優れたフェライト系ステンレス鋼材。

(5) 重量割合にて

Al: 0.003%以下, Si: 0.3~5%,
Mn: 0.2~1%, Cr: 8~25%以下

を含有するか、或いは更に

Cu: 0.05~0.8%, Ni: 0.05~0.8%,
Nb: 0.05~2.0%, Mo: 0.05~3.0%

のうちの1種以上をも含み、残部が実質的にFeであるフェライト系ステンレス鋼材に、酸化性酸又

の厚さで形成させることを特徴とする、耐錆性に優れたフェライト系ステンレス鋼材の製造方法。

3. 発明の詳細な説明

(産業上の利用分野)

この発明は、卓越した耐錆性を示すフェライト系ステンレス鋼材(鋼板等)、並びにその製造方法に関するものである。

(従来技術とその課題)

近年、高度に成長した経済環境の中で生活様式や価値観にも著しい多様化傾向が見られるようになり、例えば、高価ではあるものの、美麗かつ重厚な金属光沢と優れた耐食性を有していて独特の高級感を与えるステンレス鋼が建材その他の分野にまで広く用いられるような状況となってきた。

しかし、このようなステンレス鋼にあっても、海岸地区や火山灰降下地区等の如き厳しい環境で使用される場合には表面に所謂“しみ”と呼ばれる局所的な光沢低下や赤錆が生じるとの問題があり、“ステンレス鋼”即ち“錆なし”と言う高

は過酸化性酸溶液中浸漬及び酸溶液中電解の何れかの処理を施した後、気相メッキによって該鋼材表面にAl, Ti, Si, Nb, Cr, Mo, Cu, Ni及びこれらの窒化物並びに酸化物のうちの1種以上から成る単層又は複層の被覆層を200~30000Åの厚さで形成させることを特徴とする、耐錆性に優れたフェライト系ステンレス鋼材の製造方法。

(6) 重量割合にて

Al: 0.1~4%, Si: 0.3~5%,
Mn: 0.2~1%, Cr: 8~25%以下

を含有するか、或いは更に

Cu: 0.05~0.8%, Ni: 0.05~0.8%,
Nb: 0.05~2.0%, Mo: 0.05~3.0%

のうちの1種以上をも含み、残部が実質的にFeであるフェライト系ステンレス鋼材に、酸化性酸又は過酸化性酸溶液中浸漬及び酸溶液中電解の何れかの処理を施した後、気相メッキによって該鋼材表面にAl, Ti, Si, Nb, Cr, Mo, Cu, Ni及びこれらの窒化物並びに酸化物のうちの1種以上から成る単層又は複層の被覆層を200~30000Å

級品イメージが損なわれかねない場合が散見される。

勿論、上記問題を解決すべく、これまでも

a) 鋼の成分として耐食性向上効果の大きいCrやMo等の合金元素を添加し、ステンレス鋼自体の特性改善を図る手段。

b) 光輝焼鈍処理仕様材においては、光輝焼鈍時の露点管理を適正化して最表面に形成される酸化皮膜の耐食性向上を図る方法。

c) 同じく光輝焼鈍処理仕様材において、光輝焼鈍後に酸化性酸溶液中で不働態強化処理を施す方法。

等が提案され実用化もなされてきたが、それでも十分に満足できる成果が得られているとは言えなかった。

そこで、このような実情を踏まえての検討に基づき、「これまでの対策が“しみ”等の防止に不十分であったのは、“しみ”発生時の環境が、“しみ”形成部と言う極く狭い局所的部位に限られはするものの腐食環境が予想外の極めて厳しいものとな

るためであり、“しみ”等の発生を十分に抑制・防止するためにはステンレス鋼材最表面に従来の酸化物皮膜以上に強固な耐食性層を設ける必要がある」との結論を導き出して、

A) ステンレス鋼表面にCr等の高耐食性金属をメッキする方法、

B) ステンレス鋼表面を有機樹脂皮膜により被覆する方法(塗装法)、

等の“しみ・赤錆防止対策”を実施しようとの動きも見られた。

しかしながら、これらの対策のうち「メッキ被覆を設ける方法」は、今後更に厳しくなるであろうと予想されるメッキ廃液処理規制の点を考慮すれば工業的手法として好ましいものとは言えず、一方、「有機樹脂を塗装する方法」ではステンレス鋼の特徴である金属光沢、質感が消失してしまうので用途によっては適用できないとの問題が残るものであった。

(課題を解決するための手段)

本発明者は、上述のような観点から、特有の重

厚な金属光沢を失うことなく“しみ”や“赤錆”の問題が解決され、かつ工業生産規模での安定製造が可能な高耐錆性ステンレス鋼材を提供すべく、長年の経験の上に立って展開してきた耐食性皮膜に関する独自の知見等を加味しながら鋭意研究を重ねた結果、次に示すような新たな知見を得るに至った。即ち、

(a) 近年になって著しい進歩を遂げてきたCVD(化学蒸着法)、イオンプレーティング法、スパッタリング法等の気相メッキ法によれば、通常のメッキ法とは異なり、ステンレス鋼表面等へも容易に各種の金属、窒化物、酸化物等の薄膜を被覆することが可能となったが、この気相メッキを適用してステンレス鋼表面に特定厚さの特定物質被膜を設けると、ステンレス鋼特有の光沢が失われることなくその耐錆性が格段に改善され、“しみ”や“赤錆”の防止に著効がもたらされること、

(b) ただ、この場合、従来市販のステンレス鋼材をそのまま基材としたのでは、鋼板表面に露出している非金属介在物によってメッキ物質の純調

や気相メッキ方法の種別によらず皮膜欠陥が形成され、安定した耐錆性の改善が得られないこと、

(c) 更に、上記非金属介在物の中でも、極く普遍に見られる酸化物系非金属介在物、特にアルミナ系非金属介在物が気相メッキ皮膜の欠陥形成に最も大きな影響を及ぼしていること、

(d) ところが、鋼中のアルミナ系非金属介在物を低減するのに適正な成分を有するフェライト系ステンレス鋼材を基材とし、必要に応じてこれに“酸化性酸又は過酸化性酸溶液中への浸漬処理”或いは“酸溶液中での電解処理”を施してから前記気相メッキを施すと、優れた耐錆性を示すステンレス鋼材が極めて安定に得られること、

本発明は、上記知見等に基づいてなされたものであり、

「Al: 0.003%以下 或いは0.1~4%(以降、成分割合を变わす%は重量%とする)、

Si: 0.3~5%, Mn: 0.2~1%,

Cr: 8~25%以下

を含有し、必要に応じて更に

Cu: 0.05~0.8%, Ni: 0.05~0.8%,

Nb: 0.05~2.0%, Mo: 0.05~3.0%

のうちの1種以上をも含み、残部が実質的にFeであるフェライト系ステンレス鋼材表面に、Al, Ti, Si, Nb, Cr, Mo, Cu, Ni及びこれらの窒化物並びに酸化物のうちの1種以上から成り、かつ厚さ: 200~30000Åの単層又は複層の気相メッキ層(CVD、イオンプレーティング、スパッタリング等によるメッキ層)を設けてステンレス鋼材を構成することにより、著しく優れた耐錆性を付与した点」

に特徴を有し、更には、

「Al: 0.003%以下 或いは0.1~4%,

Si: 0.3~5%, Mn: 0.2~1%,

Cr: 8~25%以下

を含有し、必要に応じて更に

Cu: 0.05~0.8%, Ni: 0.05~0.8%,

Nb: 0.05~2.0%, Mo: 0.05~3.0%

のうちの1種以上をも含み、残部が実質的にFeであるフェライト系ステンレス鋼材を、酸化性酸又

は過酸化性酸溶液中への浸漬処理、或いは酸溶液中での電解処理に付した後、気相メッキによって該鋼材表面にAl, Ti, Si, Nb, Cr, Mo, Cu, Ni及びこれらの窒化物や酸化物のうちの1種以上から成る単層又は複層の被覆層を200~30000Åの厚さで形成させることにより、耐錆性に優れたフェライト系ステンレス鋼材を安定して製造し得るようにした点」

をも特徴とするものである。

即ち、本発明は通常のメッキ法では付与できなかった高耐食性皮膜を、気相メッキ法を適用して特定組成のフェライト系ステンレス鋼材表面上に人工的に生成させ、これによって特有の光沢を保有したままで「しみ」等の生成が極力抑えられたステンレス鋼材を実現しようとするものである。以下に、本発明に係るフェライト系ステンレス鋼材及びその製造方法を前記の如くに限定した理由と、その裏付けとなった作用を共に説明する。

(作用)

A) ステンレス鋼の成分組成

果がそれ以上に改善されないばかりか、Al多量添加に伴う熱間加工性低下が顕著となるためである。

ここで、「鋼材中のアルミナ系非金属介在物を低減させる上でAlの多量(0.1~4%)添加が有効である」との事実は感覚的には違和感を覚えるが、これはAlの特殊性に基づくものであり、Alの活量係数の変化による脱酸力低下に起因した現象によるものと考えられる。

ところで、鋼中のAl量を0.003%以下とするためには精錬終了後から造塊に至る工程でAl脱酸或いは合金元素としてのAl添加を行わないことが実際的で最も有効である。特に、Al脱酸を一切行わないことはこの種鋼材の製造においては極めて特徴的であり、かつ有利な手段である。

なお、鋼材表面に露出しているアルミナ系非金属介在物の悪影響軽減には、後述する酸化性酸溶液又は過酸化性酸溶液への自然浸漬や酸溶液中での電解処理も極めて有効である。

(a) Si

本発明ではSiは非常に重要な脱酸元素としての

(a) Al

本発明においては、鋼母材(鋼基材)中のAl含有量を0.003%以下 或いは0.1~4%の範囲内に調整することが極めて重要な要件となる。なお、望ましくは0.002%以下 或いは0.1~4%の量に調整するのが良い。なぜなら、鋼材中に生じるアルミナ系非金属介在物が鋼材表面に露出し、気相メッキの際に部分的なメッキ被膜欠陥を生じて耐食性改善効果を著しく減ずることを防止する上で、上記Al含有量調整を欠くことができないからである。

即ち、鋼母材中のAl含有量を0.003%以下に抑えるか 或いは0.1%以上に調整することによって始めてアルミナ系非金属介在物の生成を抑制し、アルミナ系非金属介在物が 鋼材表面へ露出するのを實際上問題を生じない程度に抑制することができ、鋼材の耐錆性低下を防ぐことが可能となる。なお、Al含有量を0.1%以上の範囲に調整する場合には、その上限を4%に抑えることが必要である。これは、4%を超えてAlを添加しても上記効

位置を占める。即ち、本発明に係る鋼材の溶製時には「通常の鋼材の場合に脱酸剤として多用されるAl」を有効に作用させることができないので、該溶解・精錬時の脱酸は、Alに比べて幾分作用が弱いながらもSiに依存しなければならないからである。

但し、Si含有量が5%を超えて添加されても脱酸剤としての効果がより以上に改善されないばかりか、鋼材の熱間での加工性を著しく減ずるようになる。一方、Si含有量が0.3%以下では鋼の脱酸が十分に行われぬ。従って、Si含有量は0.3~5%と定めた。

(c) Mn

Mn成分には鋼中のSを固定して熱間での加工性を確保する作用があるが、その含有量が0.2%未満では前記作用による所望の効果が得られず、一方、1%を超えて含有させることは冷間加工性や成形性の悪化につながるため、Mn含有量は0.2~1%と定めた。

(d) Cr

Crは、本発明に係る鋼母材(鋼基材)の耐食性を決定する最も重要な添加元素である。本発明鋼材の優れた耐食性は表面に設けられた気相メッキ層が大きく影響して確保されるものであるが、如何せん該メッキ層は非常に薄く、キズ付等により母材部の露出を招くことが多い。従って、このような事態に備えるためにも鋼母材においても十分な耐食性を確保しておく必要があり、この観点からCrは重要な役割を果たすものである。

しかし、Cr含有量が8%未満では鋼材キズ付部並びに鋼材端面の耐食性を十分に確保することができず、一方、大気暴露下での耐食性を問題とする本発明鋼材においては、25%を超えてCrを添加しても更なる効果の改善が明瞭でないことから、Cr含有量は8~25%と定めた。

(e) Cu, Ni, Nb及びMo

Cu, Ni, Nb及びMoは何れも鋼基材(鋼母材)の耐食性改善効果を有しているため、メッキ被膜キズ付部等での耐食性低下を防止する等の観点から必要に応じて1種又は2種以上添加される成分であ

るが、以下、それぞれの含有量限定理由を個別に詳述する。

Cu

Cuは鋼基材の耐食性改善に有効な成分であるが、その効果を明瞭とするためには0.05%以上の添加が必要であり、一方、0.8%を超えて含有させると逆に金属間化合物生成に伴う耐食性の劣化が顕在化するため、Cuを添加する場合の含有量は0.05~0.8%と定めた。

Ni

Niも、Cuと同様、耐食性改善に有効な成分であるが、その効果を明瞭とするためには0.05%以上の添加が必要であり、一方、0.8%を超えて含有させてもそれに見合うだけの耐食性向上効果が得られないことから、Niを添加する場合の含有量は0.05~0.8%と定めた。

Nb

Nbには鋼中のCを安定化する作用があり、更に鋼基材の耐食性を改善する効果を発揮するものである。特に、Cu或いはNiと共存させた場合には、

それらの相乗効果によって鋼基材の耐食性改善効果は一段と顕著になる。

そして、Nb添加によって所望の鋼中C安定化効果を確保するためには0.05%以上を含有させることが必要であるが、2.0%を超えて含有させてもC安定化効果及び耐食性改善効果が共にそれ以上に顕在化しないばかりか、逆に Laves相生成による耐食性劣化を来すことから、Nbを添加する場合の含有量は0.05~2.0%と定めた。

Mo

MoはCrと並んで耐食性改善効果の大きな添加元素であるが、その含有量が0.05%未満では耐食性改善効果が明瞭に認められず、一方、3.0%を超えて含有させても本発明鋼材が主目的とする耐食性の向上に更なる効果が認められないことから、Moを添加する場合の含有量は0.05~3.0と定めた。

(f) その他

不純物元素として鋼材中に混入してくるSは、鋼中でMo系硫化物を生成して気相メッキ時に被膜欠陥が生じるのを促すばかりでなく、母材の耐食

性そのものの劣化を招く。従って、鋼材中のS量は低い方がよい。なお、気相メッキ被膜に欠陥を生成しにくくなるレベルは0.005%以下程度であることから、鋼材中のS含有量は0.005%以下に抑えることが望ましい。

B) 気相メッキ層の厚み

気相メッキ物質としてはAl, Ti, Si, Nb, Cr, Mo, Cu及びNiの各金属、並びにこれらの窒化物や酸化物のうちの1種以上が採用でき、これらは1層だけの単層被覆として付与しても良いし、2層以上の複層として付与しても良い。

この場合、気相メッキ層の厚みが200Å未満であると均一なメッキ面(蒸着面)が得られず、メッキ層欠陥部からの耐食性劣化が顕著となる。一方、気相メッキ層の厚みが3000Åを超えた場合には鋼材曲げ部でのメッキ被膜割れやメッキ被膜剥離と言った問題が起きやすくなる。従って、気相メッキ層の厚みは200~3000Åと定めた。

なお、フェライト系ステンレス鋼材表面に欠陥

の殆んどない気相メッキ層を安定して設けるためには、前処理として酸化性酸溶液又は過酸化性酸溶液に自然浸漬したり酸溶液中で電解処理する工程を取り入れるのが良い。この前処理によって鋼材表面に露出しているアルミナ系非金属介在物が溶出してその悪影響が除かれるばかりでなく、非金属介在物の周囲が強固に不働態化されるので、該非金属介在物の存在による気相メッキ被覆鋼材の耐食性劣化が軽減される。

そして、上述のように鋼材表面へ露出したアルミナ系非金属介在物を低減・無害化するための酸化性酸溶液としては例えば“30%硝酸水溶液”等を、そして過酸化性酸溶液としては“過酸化水素水を添加した硝酸水溶液”等を推奨でき、電解処理を実施するための酸溶液も通常の電解酸洗等に適用されるものなど何れを採用しても良い。

次いで、本発明を実施例により更に具体的に説明する。

(実施例)

実施例 1

まず、第1表に示す如き、精錬過程においてA2脱酸処理を行わなかった鋼A～B及びH～K、RH炉にて非金属介在物浮上処理と真空脱酸処理を施したところの多量のA2を含有する鋼E～G、及びA2脱酸処理を行った鋼C～Dより成る各フェライト系ステンレス鋼板を準備した。

そして、これらの鋼板を60℃の30%硝酸水溶液中で電解処理して表面性状の調整（気相メッキ前処理）を行った後、スパックリングにより該表面に SiN_x ($x \approx 1.35$)を600Åの厚みでメッキした。なお、スパックリング処理に際しては鋼板基板を300℃に加熱保持した。

続いて、このようにして製造された各フェライト系ステンレス鋼板から試験片を2個ずつ採取して孔食電位を測定すると共に、その耐腐性評価を行い、これらの結果をまとめて第2表に示した。なお、耐腐性の評価は第3表に示す基準に従って行い、第2表には相当する評点を記入した。

第2表に示される結果からも明らかなように、本発明に係るフェライト系ステンレス鋼板は何れ

第 1 表

鋼 種		化 学 成 分 (重量%)											
		C	Si	Mn	P	S	Cr	Al	Cu	Ni	Nb	Mo	Fe及び不純物
本発明対象鋼	A	0.002	0.52	0.35	0.020	0.001	19.2	0.001	0.03	0.03	—	—	残
	B	0.003	0.55	0.32	0.026	0.001	19.2	0.001	0.51	0.24	—	—	残
比 較 鋼	C	0.005	0.34	0.18	0.026	0.002	18.9	0.006	0.47	0.22	—	—	残
	D	0.004	0.36	0.18	0.026	0.001	19.0	0.077	0.47	0.20	—	—	残
本発明対象鋼	E	0.002	0.47	0.33	0.025	0.001	18.9	0.121	0.48	0.20	—	—	残
	F	0.005	0.52	0.32	0.026	0.002	19.1	0.98	0.48	0.21	—	—	残
	G	0.004	0.53	0.32	0.025	0.001	19.1	2.49	0.49	0.18	—	—	残
	H	0.003	0.48	0.30	0.020	0.001	19.2	0.001	0.52	0.02	—	—	残
	I	0.001	0.50	0.32	0.021	0.001	19.2	0.001	0.03	0.50	—	—	残
	J	0.004	0.50	0.31	0.021	0.001	19.3	0.001	0.04	0.02	0.53	—	残
	K	0.002	0.51	0.33	0.021	0.001	19.3	0.001	0.03	0.03	—	2.11	残

(注) *印は、本発明で規定する条件から外れていることを示す。

第 2 表

試験番号		供試鋼	気相メッキ (還元)物質	メッキ 処理の 有無	メッキ層 の厚み (μ)	スパックリング 時 の基板温度 ($^{\circ}$ C)	孔食電位 (60 \pm 0.01N H ₂ SO ₄ 中(対SCE))		耐蝕性 (6ヵ月同大気暴露後の評点)	
							第1試験片	第2試験片	第1試験片	第2試験片
本発明例	1	A	SiN ₄		600	300	>900 mV	>900 mV	10	10
	2	B					>900 mV	>900 mV	10	10
比較例	3	C					364 mV	433 mV	4	4
	4	D					565 mV	399 mV	4	4
本発明例	5	E					>900 mV	>900 mV	10	10
	6	F					>900 mV	>900 mV	10	10
	7	G					>900 mV	>900 mV	10	10
	8	H					>900 mV	>900 mV	10	10
	9	I					>900 mV	>900 mV	10	10
	10	J					>900 mV	>900 mV	10	10
	11	K					>900 mV	>900 mV	10	10

(注) *印は、本発明で規定する条件から外れていることを示す。

第 3 表

耐蝕性の評点	大気暴露試験による発錆の程度	耐蝕性の評点	大気暴露試験による発錆の程度
10	発錆なし	5	赤錆の軽微な点錆
9	極く軽微な“しみ”	4	赤錆点錆
8	極く軽微な“しみ”	3	赤錆点錆
7	軽微な“しみ”	2	全面赤錆点錆
6	軽微な“しみ”	1	全面赤錆

も優れた耐蝕性を示すのに対して、基材鋼板の成分組成が本発明で規定する条件から外れている比較例3及び4によるものでは耐蝕性が著しく劣ることが分かる。

なお、Al脱酸した鋼を適用した比較例3及び4によるものでは、基材鋼板に圧延方向へ長く連なったアルミナ系非金属介在物が“線状非金属介在物群”として多数認められ、スパックリング後の表面観察においてもアルミナ系非金属介在物に起因した複数の皮膜欠陥が観察された。

しかるに、本発明例5～7によるものは、基材鋼板が0.121～2.49%と多量のAlを含有しているにも係わらず良好な結果が得られているが、これはAlの多量添加に伴う“Alの脱酸力低下現象”によってアルミナ系非金属介在物の生成が減少するためと推察される。実際、基材鋼板中のアルミナ系非金属介在物は、積極的なAl脱酸を行わなかった鋼の適用になる本発明例1～2及び8～11のそれと同等レベルであった。

また、これらの試験結果からは、「基材鋼板中

のAl量を特定範囲に調整すると言う工業的に可能な手段により、気相メッキ鋼板の耐蝕性に影響を及ぼさないレベルで鋼中のアルミナ系非金属介在物を必要かつ十分にコントロールすることができる」点もが確認される。

実施例 2

Al脱酸を行わず、RH炉を用いて非金属介在物の浮上促進と真空脱酸処理を行った第4表に示す鋼により成るフェライト系ステンレス鋼板を準備した。

次に、該鋼板から複数の試験片を切り出し、第5表に示す如く一部を除いて脱脂処理した後、スパックリングにより接表面にSiO₂(x=2)を種々の厚みでメッキした。なお、スパックリング処理に際して鋼板基板は300 $^{\circ}$ Cに加熱保持された。

このようにして製造された気相メッキフェライト系ステンレス鋼板について、実施例1と同様に孔食電位の測定と耐蝕性評価を行うと共に、10t曲げ時における気相メッキ被膜の割れ状況を調査したが、その結果を第5表に併せて示した。

第 4 表

鋼 種		化 学 成 分 (重量%)										
		C	Si	Mn	P	S	Cr	Al	Cu	Ni	Nb	Mo
本発明対象鋼	L	0.012	0.53	0.28	0.028	0.002	9.8	0.001	0.52	0.15	—	—
												Fe及び不純物
												残

第 5 表

試験 番号	供 試 鋼	気相メ ッキ(蒸着) 物質	メッキ 前処理 の有無	メッキ層の 厚み (μ)	スパッタリング時 の基板温度 ($^{\circ}$ C)	孔食電位 (60 $^{\circ}$ C 0.01N NaCl 中 (対SCE))		耐腐性 (6ヶ月間大気暴露後の評点)		10:1曲げ部割れ
						第1試験片	第2試験片	第1試験片	第2試験片	
比 較 例 12			無	40		40 mV	43 mV	2	1	なし
13				80		242 mV	258 mV	5	5	なし
14				80		381 mV	423 mV	6	6	なし
15				200		687 mV	705 mV	9	9	なし
16				400		879 mV	>900 mV	9	10	なし
17				800		>900 mV	>900 mV	10	10	なし
18				1500		>900 mV	>900 mV	10	10	なし
19				4000		>900 mV	>900 mV	10	10	微小ミクロ割れ
20				8000		>900 mV	>900 mV	10	10	微小ミクロ割れ
21				15000		>900 mV	>900 mV	10	10	微小ミクロ割れ
22				28000		>900 mV	>900 mV	10	10	微小ミクロ割れ
比 23				>32000		>900 mV	>900 mV	10	10	割れ大

(注1) 「比」は「比較例」を要す。

(注2) *印は、本発明で規定する条件から外れていることを示す。

第5表に示される結果からも、本発明に係るフェライト系ステンレス鋼板は何れも優れた耐腐性を示すのに対して、気相メッキ被膜の厚さが本発明での規定値から外れている比較例12~13及び23によるものでは耐腐性が著しく劣るか、或いは成形加工時に被膜割れを生じやすいことが明らかである。

なお、スパッタリングによると基材鋼板上へのSiO₂の蒸着は島状に開始して均一には進行せず、島状状態から次第に全面へと進行して行く過程をたどるものと見られるが、本実施例においてもその傾向が認められ、蒸着膜厚(メッキ膜厚)が薄い場合には「蒸着膜の欠陥に起因すると推察される耐腐性改善レベルの低下傾向」が見られた。そして、この傾向は蒸着基板(基材鋼板)の温度を高めることにより或る程度は改善されるものと期待されたが、実際にはそれほど大きな改善はなく、およそ200 μ mの膜厚を境により耐腐性が安定して良好となった。このことは、他の気相メッキ物質(蒸着物質)を使用した場合にも大差なかった。

また、蒸着膜厚(メッキ膜厚)が厚くなるに従って蒸着時と放冷後の温度差並びに気相メッキ物質(蒸着物質)の内部応力によると思われる気相メッキ被膜の割れが生じやすくなり、特に30000 μ mを超えた膜厚ではこの傾向が顕著となって実用には耐えないレベルとなることも確認された。

なお、気相メッキ被膜の密着性にはスパッタリング前の脱脂処理の影響も大きく、脱脂を十分に行う必要のあることが分かった。

実施例 3

第6表に示す如き、精錬過程においてAl脱酸処理を行った鋼M、並びにAl脱酸処理を行わなかった鋼N~Pより成る各フェライト系ステンレス鋼板を準備した。

次に、これらの鋼板を60 $^{\circ}$ Cの30%硝酸水溶液中に浸漬処理して表面性状の調整(気相メッキ前処理)を行った後、スパッタリングによって該表面に第7表で示す如き各種メッキを施した。なお、スパッタリング処理に際してはこれまでの例と同じく鋼板基板を300 $^{\circ}$ Cに加熱保持した。

第 6 表

鋼 種		化 学 成 分 (重量%)											
		C	Si	Mn	P	S	Cr	Al	Cu	Ni	Nb	Mo	Fe及び不純物
比 較 鋼	M	0.005	0.28	0.16	0.025	0.002	16.8	0.008	0.03	0.03	—	—	残
本発明対象鋼	N	0.005	0.53	0.35	0.025	0.001	16.8	0.001	0.08	0.02	—	—	残
	O	0.005	0.51	0.33	0.027	0.001	20.3	0.001	0.53	0.08	0.53	0.82	残
	P	0.004	0.53	0.29	0.026	0.001	22.3	0.001	0.51	0.45	0.55	1.13	残

(注) *印は、本発明で規定する条件から外れていることを示す。

第 7 表

試験番号		供試鋼	気相ノッキ(蒸着)物質	ノッキ層の厚み(Å)	気相ノッキ時の基板温度(℃)	孔食電位 (60℃の0.01N NaCl中(対SCE))		耐腐性 (6ヵ月間大気暴露後の評点)	
						第1試験片	第2試験片	第1試験片	第2試験片
比較例	24	M	SiO ₂	400	300	0.33 V	0.28 V	4	3
	25		(下層)Ni, (上層)SiO ₂	1000		0.35 V	0.38 V	5	5
	26		(下層)Co, (上層)SiO ₂	600		0.36 V	0.33 V	4	4
	27		(下層)Ni, (上層)TiN	500		0.39 V	0.42 V	5	4
	28		Nb-NbO ₂	1000		0.56 V	0.36 V	4	5
	29		(下層)Cr, (上層)Mo	800		0.53 V	0.63 V	6	5
本発明例	30	N	SiO ₂	400		0.89 V	> 0.9 V	10	10
	31		(下層)Ni, (上層)SiO ₂	450		> 0.9 V	> 0.9 V	10	10
	32		(下層)Co, (上層)SiO ₂	600		> 0.9 V	> 0.9 V	10	10
	33		(下層)Ni, (上層)SiN	450		> 0.9 V	> 0.9 V	10	10
	34		(下層)Co, (上層)SiN	600		> 0.9 V	> 0.9 V	10	10
	35		(下層)Ni, (上層)TiN	500		> 0.9 V	> 0.9 V	10	10
	36		Nb-NbO ₂	1000		> 0.9 V	> 0.9 V	10	10
	37	(下層)Cr, (上層)Mo	800	> 0.83 V		> 0.85 V	10	10	
	38	O	(下層)Cr-Mo, (上層)Nb-NbO ₂	1200		> 0.9 V	> 0.9 V	10	10
	39		(下層)Co-CoO ₂ , (上層)Nb-NbO ₂			> 0.9 V	> 0.9 V	10	10
	40		(下層)Al, (中間層)Al-AlO _x , (上層)AlO ₂	6000		> 0.9 V	> 0.9 V	10	10
	41	P	Cr	5000		> 0.88 V	0.86 V	10	10
	42		Ti			> 0.9 V	> 0.9 V	10	10

(注) *印は、本発明で規定する条件から外れていることを示す。

続いて、このようにして製造された各フェライト系ステンレス鋼板につき、実施例1と同様に孔食電位測定と耐錆性評価を行い、これらの結果をまとめて第7表に示した。

第7表に示される結果からも明らかなように、本発明に係るフェライト系ステンレス鋼板は何れも優れた耐錆性を示すのに対して、基材鋼板の成分組成やメッキ被膜の厚さが本発明で規定する条件から外れている比較例24~29によるものでは耐錆性が著しく劣ることが分かる。

なお、メッキ層(蒸着物質)の腐蝕化は、気相メッキフェライト系ステンレス鋼板の耐食性改善に対して相乗効果を奏するばかりではなく、蒸着物質の密着性改善に対しても効果を有することが確認され、特にNi又はCoの下層を設けるのが有効であることも分かった。

更に、上記各実施例においては気相メッキ手段としてスパッタリングを適用したもののみを示したが、他の蒸着手段としてCVDやイオンプレーティングを適用した場合にも同様に良好な結果が

得られることをも確認した。

(効果の総括)

以上に説明した如く、この発明によれば、従来材に比べて格段に優れた耐錆性を有し、自動車用モール材、外装用建材、内装用建材等の幅広い分野に適用してそれらの価値や機能の著しい改善が期待される高耐錆性フェライト系ステンレス鋼材を安定して提供することが可能となるなど、産業上極めて有用な効果がもたらされる。

出願人 住友金属工業株式会社

代理人 弁理士 今 井 殷